Computation of the Spatial Locations of Atoms of a Chain Molecule Undergoing Intramolecular Rotations

IN connection with an investigation of intramolecular factors affecting the vibration of the hydroxyl group[1] it was desired to find the relative positions of the atoms of a molecule for a large number of rotational isomers. Atom locations have been calculated[2] by using multiple transformations of coordinate systems. This was tried, but it was found that fewer computational steps are necessary when using interrelations among direction cosines in a single coordinate system.

For any arbitrary locations of atoms A, B, C (Fig. 1), the basic computational unit determines the coordinates of atom D in terms of given bond lengths and angles. In the equations which follow, the subscript i takes on the values 0, 1, 2 (using arithmetic modulo 3), so that each equation shown becomes three equations in the three Cartesian coordinates. C_i and D_i are coordinates of atoms C and D, respectively. Greek letters are direction cosines of directed lines as shown in Fig. 1. The basic computational unit consists of four steps: (1) Compute direction cosines of directed line **BF** perpendicular to both **AB** and **BC**.

$$\lambda_i=(\alpha_{i+1}\beta_{i+2}-\beta_{i+1}\alpha_{i+2})/\sin V_B \qquad (i=0, 1, 2).$$

(2) Compute direction cosines of **BG**, perpendicular to **BC** and making angle J with **BF**.

$$\mu_i=\lambda_i\cos J+(\lambda_{i+1}\beta_{i+2}-\beta_{i+1}\lambda_{i+2})\sin J \qquad (i=0, 1, 2).$$

CG′ is a line through C parallel to **BG**.

(3) Compute direction cosines of **CD**, perpendicular to **CG′** and making angle V_c with the extension of **BC**.

$$\gamma_i=\beta_i\cos V_c+(\beta_{i+1}\mu_{i+2}-\mu_{i+1}\beta_{i+2})\sin V_c \qquad (i=0, 1, 2).$$

(4) From these direction cosines, bond length L, and coordinates of atom C, compute coordinates of atom D.

$$D_i=C_i+L\gamma_i \qquad (i=0, 1, 2).$$

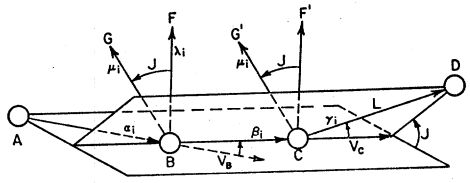

FIG. 1. Directed lines and angles used in basic computational unit for calculating location of atom D from information about atoms A, B, C. Subscript i takes on the values 0, 1, 2 to give three direction cosines for each Greek letter.

After obtaining coordinates of atom D, relabel atoms B, C, D as A, B, C, and compute coordinates of the next atom by repeating the procedure with new values of V, L, J. This basic computational unit can then be iterated to cover all atoms in a molecule for any set of bond lengths and angles. Internal rotation corresponds to recomputing the molecule with new J's while keeping V's and L's constant. If restricted rotation is assumed, only a limited number of values of each J need be used.

This computation has been programmed for a digital computer for a chain molecule. Flow diagrams are available on request. Modifications of the iteration procedure would make it applicable to branched and cyclic molecules.

I am indebted to Elizabeth A. Eddy for helpful assistance in programming the computation for a Bendix G-15D computer[3] and to Kenneth A. Tabler for trying it out on an IBM 1620.[3]

* Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[1] C. R. Eddy, J. S. Showell, and T. E. Zell, J. Am. Oil Chemists' Soc. (to be published).

[2] H. Eyring, Phys. Rev. **39**, 746 (1932); T. Shimanouchi and S. Mizushima, J. Chem. Phys. **23**, 707 (1955); R. H. Schwendeman, J. Mol. Spectroscopy **6**, 301 (1961).

[3] Mention of specific commercial products does not imply endorsement by the U. S. Department of Agriculture over others of a similar nature not named.